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THE CHEMISTRY AND APPLICATIONS FOR THE
SOLUBILIZATION OF CHROMATE SALTS IN
NONPOLAR ORGANIC MEDIA. PART I.

Jack Ohr, et al

Naval Air Development Center
Warminster, Pennsylvania

5 March 1974

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) For the first time, potassium chromate has been dissolved in significant concentrations in nonpolar organic solvents with the aid of the macrocyclic polyether complexing agents first investigated by Dodersen. When a two phase system of chromate in water and polyether in organic solvent is agitated, the fraction of salt which is complexed into the organic phase is found to be inversely dependent on the pH of the aqueous phase. This suggests that some chromium species are more compatible than others as		

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anionic partners with the complexed potassium ion. The data indicates that this species is bichromate (HCrO_4^-), and that in solution each bichromate anion is arrayed in an ordered fashion with a single complexed potassium cation.

Application of this chemistry towards improving organic materials shows promise. TT-E-489F alkyd enamels containing small amounts of dissolved chromate show marked superiority over unmodified enamels in protecting aluminum, steel, and magnesium surfaces from the corrosive effects of long term 5% salt spray exposure.

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S U M M A R Y

INTRODUCTION

In 1967 Pedersen reported the synthesis of certain macrocyclic polyethers capable of forming stable complexes with the alkali metal cations⁽¹⁾⁻⁽⁶⁾. As a consequence, it then became possible to solubilize highly ionic alkali salts into nonpolar organic solvents, provided that the anion was polarizable enough to be compatible with the solvent. Accordingly, it was of interest for this Laboratory to pursue the goal of solubilizing the highly effective corrosion inhibitor, potassium chromate, into organic media characteristic of aircraft materials. Unfortunately, the chromate anion is too "hard" for compatibility in such media, as may be predicted by analogy with other hard bases. This report deals with the chemistry which we found to be effective for circumventing this obstacle. The practical implications of successfully dissolving potassium chromate in organic materials is discussed.

The work reported herein was conducted under Task No. ZF61412001, IZO Work Unit No. GC312.

SUMMARY OF RESULTS

1. When a two phase system of potassium chromate in water and polyether in organic solvent is agitated, the fraction of salt which is complexed into the organic phase is found to be inversely dependent on the pH of the aqueous phase.
2. High concentrations of the complex are prepared by solvent evaporation of the organic phase.
3. Addition of the concentrated soluble chromate complex to alkyd enamel topcoat results in improved salt spray exposure tests.

-
- (1) C. J. Pedersen, J. Am. Chem. Soc., 89, 2495 (1967)
 - (2) C. J. Pedersen, J. Am. Chem. Soc., 89, 7017 (1967)
 - (3) C. J. Pedersen, J. Am. Chem. Soc., 92, 386 (1970)
 - (4) C. J. Pedersen, J. Am. Chem. Soc., 92, 391 (1970)
 - (5) C. J. Pedersen, Fed. Proc. 27, 1305 (1968)
 - (6) C. J. Pedersen and H. K. Frensdorff, Angew. Chem. Internat. Ed., Vol. 2, No. 1, pp 16-25 (1972); and references therein

CONCLUSIONS

1. The pH dependency of the complex formation is explained by dissociation and hydrolysis equilibria of the Cr VI anions.
2. Complexed chromate provides corrosion protection by (1) leaching from the coating, (2) chemically altering (possibly curing by oxidation) the coating and/or (3) increased adhesion of the coating to the substrate.

RECOMMENDATIONS

None at this state of research.

FUTURE WORK

1. The synthesis of the more efficient complexing agent 18-Crown-6 and subsequent evaluation is planned.
2. Topcoat characteristics in addition to salt spray exposure will be examined; i.e., yellowing, weatherability, etc.
3. Application of soluble chromate chemistry to other organic coatings and fluids will be examined.

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BACKGROUND

1. Complexing of sodium, potassium, and related cations by neutral molecules is an uncommon phenomenon. Strong stoichiometric complexes have been observed only in the last decade, and then only with biological materials. ⁽⁷⁾⁽⁸⁾

Hence, some of the recently synthesized macrocyclic polyethers have aroused considerable interest in several divisions of chemistry because they form stable complexes, both in solution and in the crystalline form, with salts of alkali and other metals. The polyethers are neutral compounds containing four to twenty oxygen atoms each separated from the next by two or more carbon atoms, but the most effective complexing agents are found among those containing five to ten oxygen atoms each separated from the next by two carbon atoms. These compounds form 1:1 (but sometimes 2:1 and 3:2) salt : polyether complexes in which the cation is encircled by the oxygen atoms of the polyether ring, being held there by the electrostatic attraction between the negatively charged oxygens of the C-O dipoles and the cation.

2. The most spectacular way in which complexing by cyclic polyethers manifests itself is the solubilization of ionic compounds in organic solvents. The reason for this is that these macrocycles are able to accommodate a limited amount of salt in complex form. Little difficulty is presented by the cation in this account (as long as it is a good fit within the macrocyclic ring in which it is housed) since it is surrounded by organophilic groups. However, interaction between the anion and a nonpolar solvent is much less favorable, especially for small anions of high charge density and low polarizability. ⁽⁹⁾ Accordingly, salts of such "hard" anions as fluoride or sulfate are often not solubilized appreciably by cyclic polyethers, while those of "soft" anions such as iodide and fatty acid anions are solubilized more easily.

3. Although several simple salts had already been solubilized in organic solvents by macrocyclic complexation at the time this research was begun ⁽¹⁾⁽²⁾⁽³⁾⁽⁴⁾

(7) Z. Stefancic and W. Simon, *Microchem. J.* 12, 125 (1967)

(8) L. A. R. Pioda, H. A. Wachter, R. E. Dehnor, and W. Simon, *Helv. Chim. Acta* 50, 1373 (1967)

(9) R. G. Farnson, *Science*, 151, 172 (1966)

it was by no means assured that this success was extrapolative to the chromates. The reason is that the chromate anion is considered to be "hard" in the sense of a relatively non-polarizable electronic shell, and therefore, incompatible with the "soft" organic cation. Potassium chromate was the salt employed for this research. Two macrocyclic polyethers were used:

- a. 2,3,11,12-Dibenzo-1,4,7,10,13,16-hexaoxacyclooctadeca-2,11-diene. This compound is known more simply in the literature as Dibenzo-18-crown-6. It will be referred to in this report as DEC.
- b. 2,5,8,15,18,21-Hexaoxatricyclo 20.4.0.0^{9,14}-hexacosane. This compound is also known as Dicyclohexyl-18-Crown-6 and will be referred to herein as DCC.

Both compounds were chosen for this work since their eighteen-atom rings provide an optimal fit for the potassium cation. Figures 1 and 2 show configurations for DEC and DCC respectively. Figure 3 is a photo of a Fisher-Hirschfelder-Taylor molecular model of potassium bichromate complexed with DEC. The potassium cation may be found in its postulated position at the center of the macrocyclic ring. The moiety outside the ring is the bichromate anion (as will be demonstrated herein), however, its actual position with respect to the ring is only tentative.

4. The purpose of the investigation reported herein was to utilize the principles of the new chemistry toward improving the material science field of corrosion protection of aircraft metals. Specifically, research was to be directed to solubilizing the highly effective corrosion inhibiting chromate salts in organic nonpolar solvents representative of aircraft materials, and to explore the practical implications therefrom. Chromate salts are among the best corrosion inhibitors for aircraft metals.⁽¹⁰⁾ However, they are insoluble in nonpolar solvents. In order for chromates to be effective in paints, for example, they must be dispersed throughout the vehicle by milling at high concentrations in order to minimize the distance between each vehicle-encapsulated salt clump in the dry film. This continuity is necessary to

(10) M. H. Uhlig, Corrosion and Corrosion Control, 2nd ed., John Wiley and Sons, New York (1971)

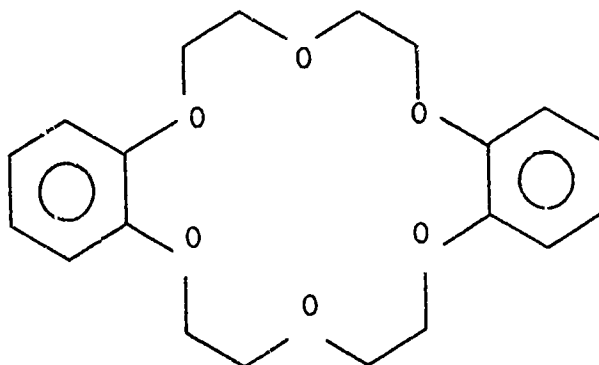


Figure 1. Dibenzo-18-crown-6

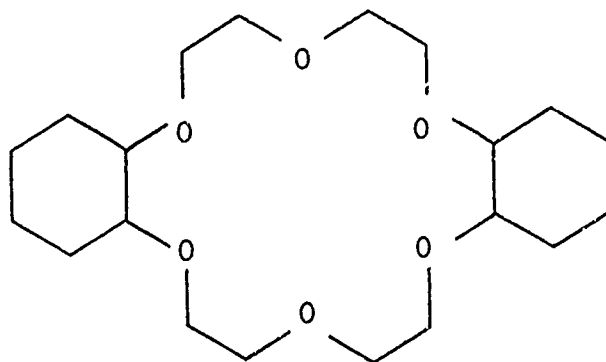


Figure 2. Dicyclohexyl-18-crown-6

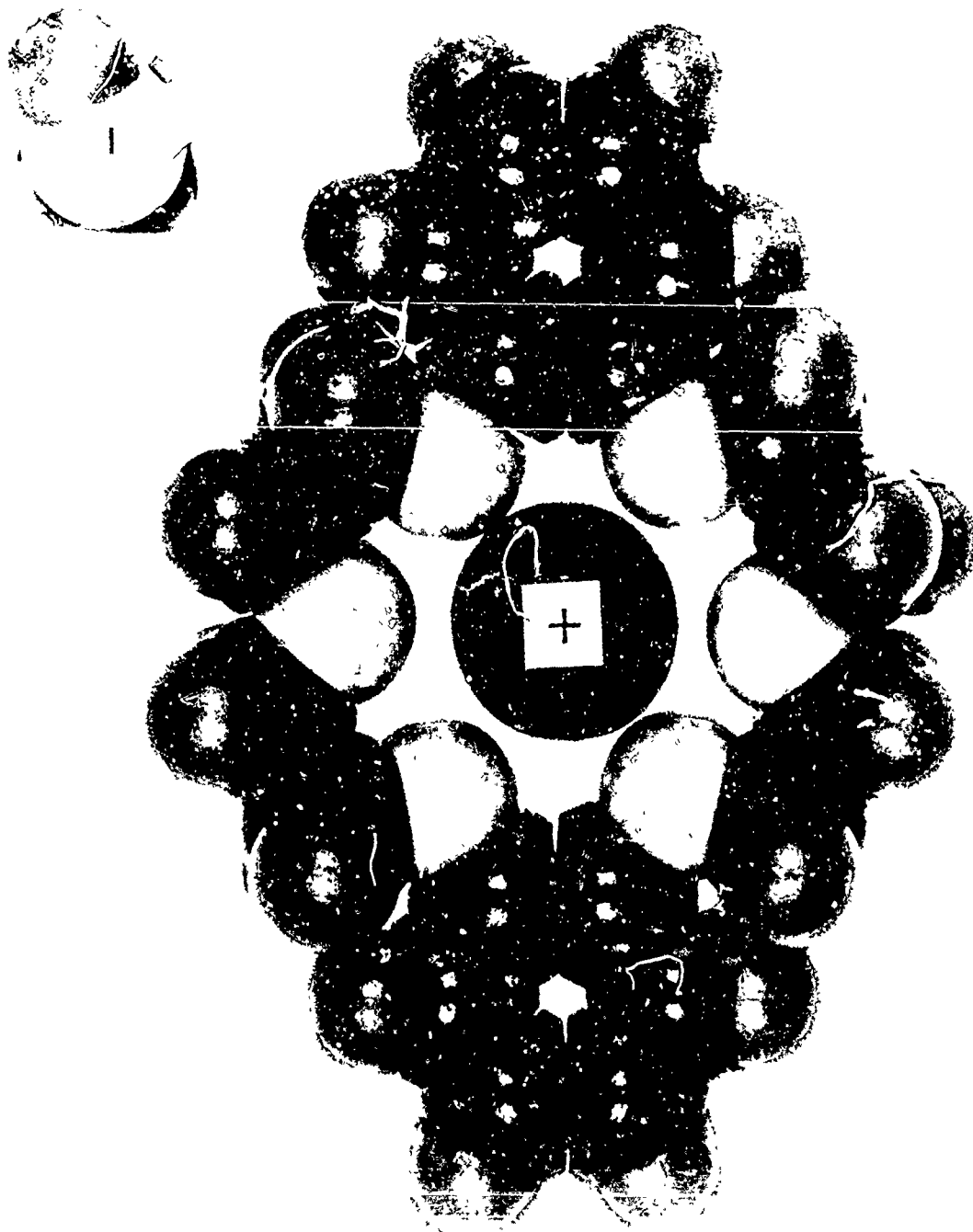


Figure 3. Molecular Model of DBC - Potassium Bichromate Complex

maintain long-term leaching of the chromate from the dry film to the potential corrosion area. These high salt levels produce flat yellow coatings suitable for use only as primer coatings.

5. Envisaged as one of the practical objectives of this research is the immediate conversion of a wet paint topcoat in any non-white color to an effective corrosion inhibiting coating by the addition of a small quantity of soluble complexed chromate; small enough not to affect the color of non-white coatings but sufficient to insure satisfactory corrosion protection without the added costs and labor of primer application. It is noteworthy that the critical concentration for the protection of steel by chromates has been determined to be as low as 10^{-3} to 10^{-4} molar.⁽¹⁰⁾ Even at very low concentrations, the solubilized chromate salt will be distributed homogeneously throughout the dry film by virtue of its dissolution in the medium (as opposed to dispersion), and therefore, will insure the availability of chromate throughout the thickness of the film. Topcoatings which would be candidates for modification are those whose films exhibit satisfactory adhesion to metals without the intermediacy of primer. Generally, these will be non-specular coatings although some gloss alkyd enamels—especially those which require baking—will also be suitable.

6. It is desired to differentiate this research from the field of "organic chromates" which have become known as corrosion inhibitors for paint primers and other uses. Organic chromates are generally separated into three categories:⁽¹¹⁾ (1) chromic (or dichromic) acid esters of organic alcohols, (2) quaternary ammonium salts of chromic (or dichromic) acid, and (3) mixtures of amine bases and inorganic chromates or dichromates. The compounds of (1) and (2) have been known for a long time. Aniline and guanidine salts were made over seventy years ago. However, the use of these salts as corrosion inhibitors has occurred within the last twenty years, and most of the

(11) D. S. Young, Paint and Varnish Prod., 35-38, July (1971)

references are from eastern Europe, especially the Soviet Union. (12)-(17) incl. Some of the deficiencies of compounds (1) and (2) for paint use have been found to be as follows: retardation of drying rates in enamel (curing) types of coatings, blistering of the dry films during service life, deterioration of the film if baking is required, (18) and gelation of the wet paint during storage. These defects are especially prominent for the quaternary salts. (18) The third category of materials was developed within the last decade to obviate these drawbacks and success has been reported with them. However, these mixtures do not form solutions but dispersions when added to paints and, therefore, would require more chromate to achieve equivalent corrosion protection. Accordingly, this report deals with research to find new sources of chromates for the materials protection field which would be soluble in low polarity media without the disadvantages noted for the organic chromates. As already noted, the approach taken was in the new field of macrocyclic polyether complexation.

RESULTS

A brief outline of experimental procedures and symbols is presented to facilitate the reading of this Section and the Discussion which follows; a detailed account may be found under Experimental.

A 0.5 M solution of potassium chromate in water, adjusted to the desired pH with HCl, is placed in contact with a 10^{-3} M solution of polyether in methylene chloride in a separatory funnel. The aqueous phase will be designated Solution #1 and the organic, Solution #2. When these two solutions are brought into equilibrium with sufficient agitation, some hexavalent chromium specie. (hereinafter called Cr +6) is complexed and transferred to

(12) C. K. Sloan, U. S. Patent 2,270,386 (1939)

(13) Zhurnal Prikladnoi Khimii, 33, 1594-99 (1960)

(14) Lakokracochnye Materialy, 3, 15-21 (1962)

(15) French Patents 83,001 and 1,359,621

(16) British Patents 1,122,003 and 1,123,642

(17) U. S. Patent 3,598,616 (1971)

(18) Private Communication with Mr. D. S. Young

the organic phase. In order to know the fraction of Cr +6 thus transferred (complexed), the complex must be decomposed and completely extracted into an aqueous phase for analysis; this is easily done by shaking Solution #2 with distilled water. The final Cr +6 aqueous phase is designated Solution #3.

1. Potassium chromate is soluble in methylene chloride or benzene with the aid of polyethers DCC or DEC (causing the organic phase to appear light yellow to deep orange depending upon the polyether and Cr +6 concentrations employed). In addition, solubility is an inverse function of the pH of Solution #1.

2. Complexation between the Cr +6 species and polyether is indicated by UV spectra in Figures 4 and 5 which show DEC before and after contact with Solution #1. The "after" situation shows the formation of a new absorption peak (indicative of complex formation) about six millimicrons to the long wavelength side of the major peak at 273 nm and a new broad band from about 330 to 390 nm resulting from absorption by the Cr +6 species.

3. When DEC is employed and the pH of Solution #1 is below 2.0, an analysis of Solution #3 indicates that one atom of Cr +6 is present therein for each molecule of polyether used in Solution #2; i.e., 100% complexation.

4. Solutions of at least 1.0 M Cr +6 in methylene chloride are readily prepared by flash evaporation of an organic solution with a high complexation percentage.

5. DCC is superior to DEC as a complexation agent for Cr +6 since at a given pH (below 7) a significantly higher fraction of the Cr +6 enters into complexation with DCC than with DEC, as shown in Figure 6.

6. Figure 7 shows a moderate degree of structure ⁽¹⁹⁾ in the UV band from 320 to 400 nm for the Cr +6 - DEC complex in methylene chloride whereas Figure 8 shows a smooth band in the same region for Cr +6 in aqueous solution. This suggests that in solution each Cr +6 anion is oriented in a definite way

(19) L. W. Johnson and S. P. McGlynn, Chemical Physics Ltrs, 7, 618 (1970)

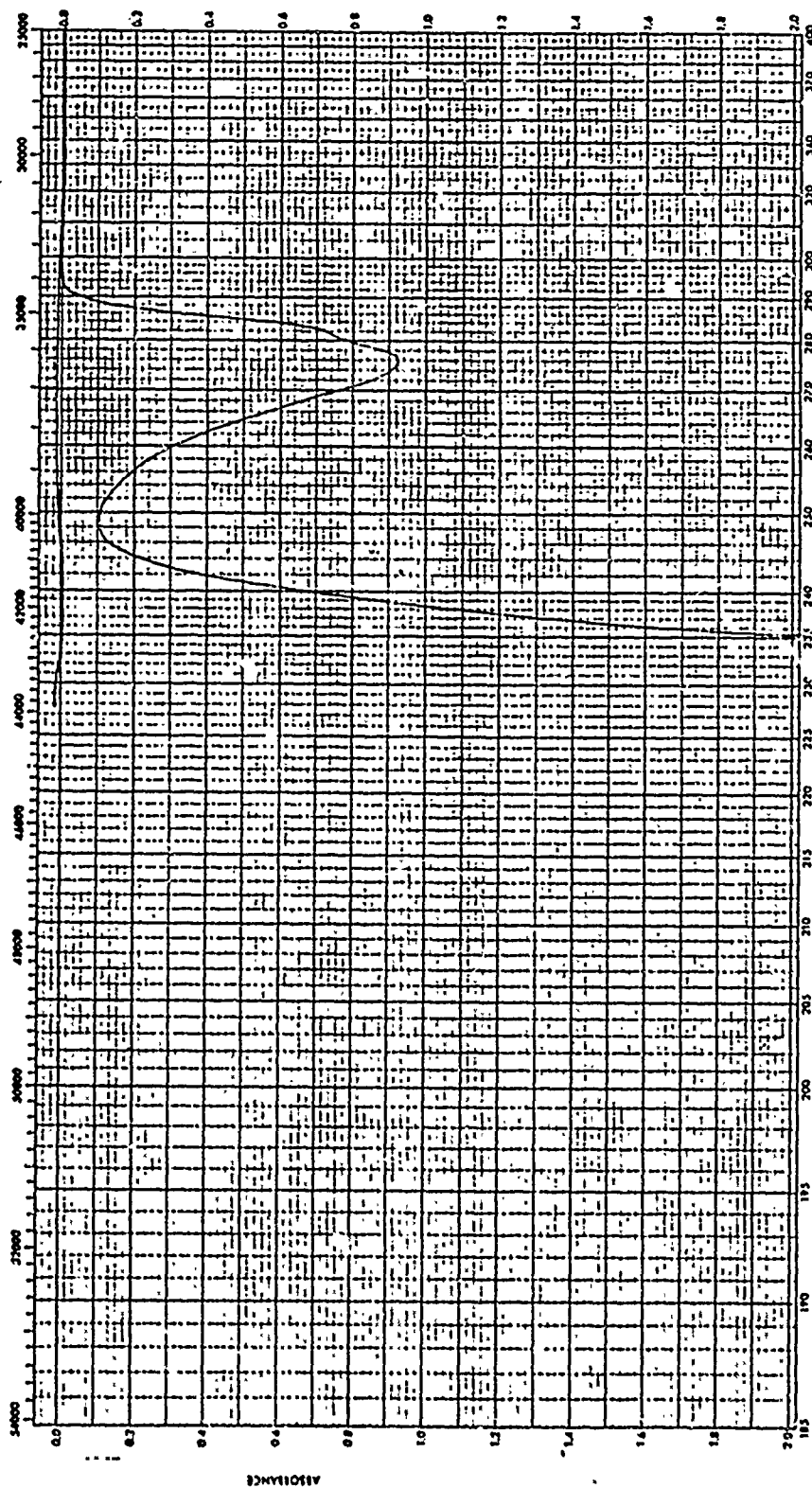


Figure 4. UV Spectrum of Dibenzot-18-crown-6 in Methylene Chloride,
Concentration 1.5×10^{-4} M.

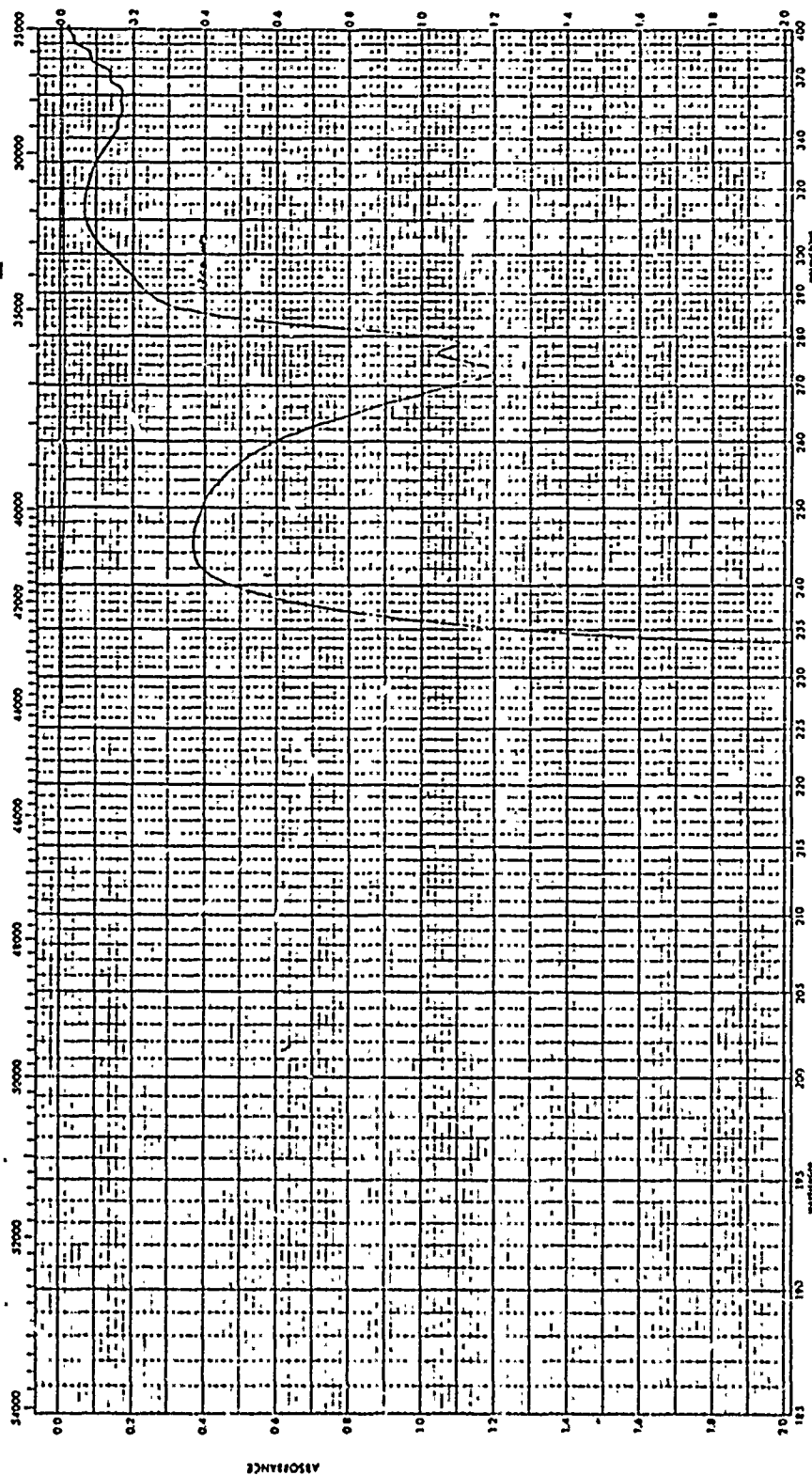


Figure 5. UV Spectrum of Dibenzo-18-crown-6 Complex in Methylene Chloride, Concentration 1.5×10^{-4} M.

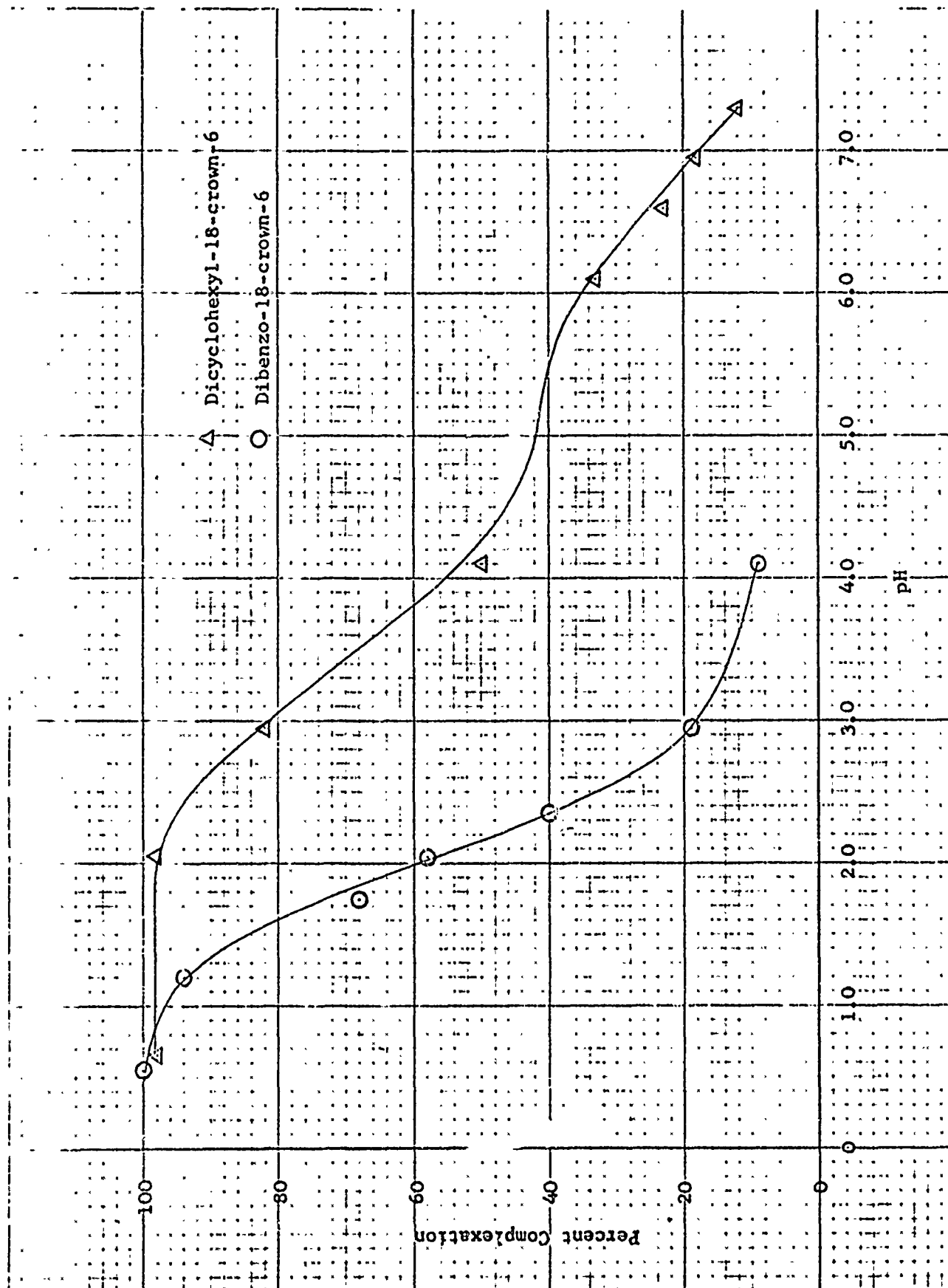


Figure 6. Percent Complexation of Cr +6 by DBC and DCC as a function of pH, Polyether Concentration 1.0×10^{-3} .

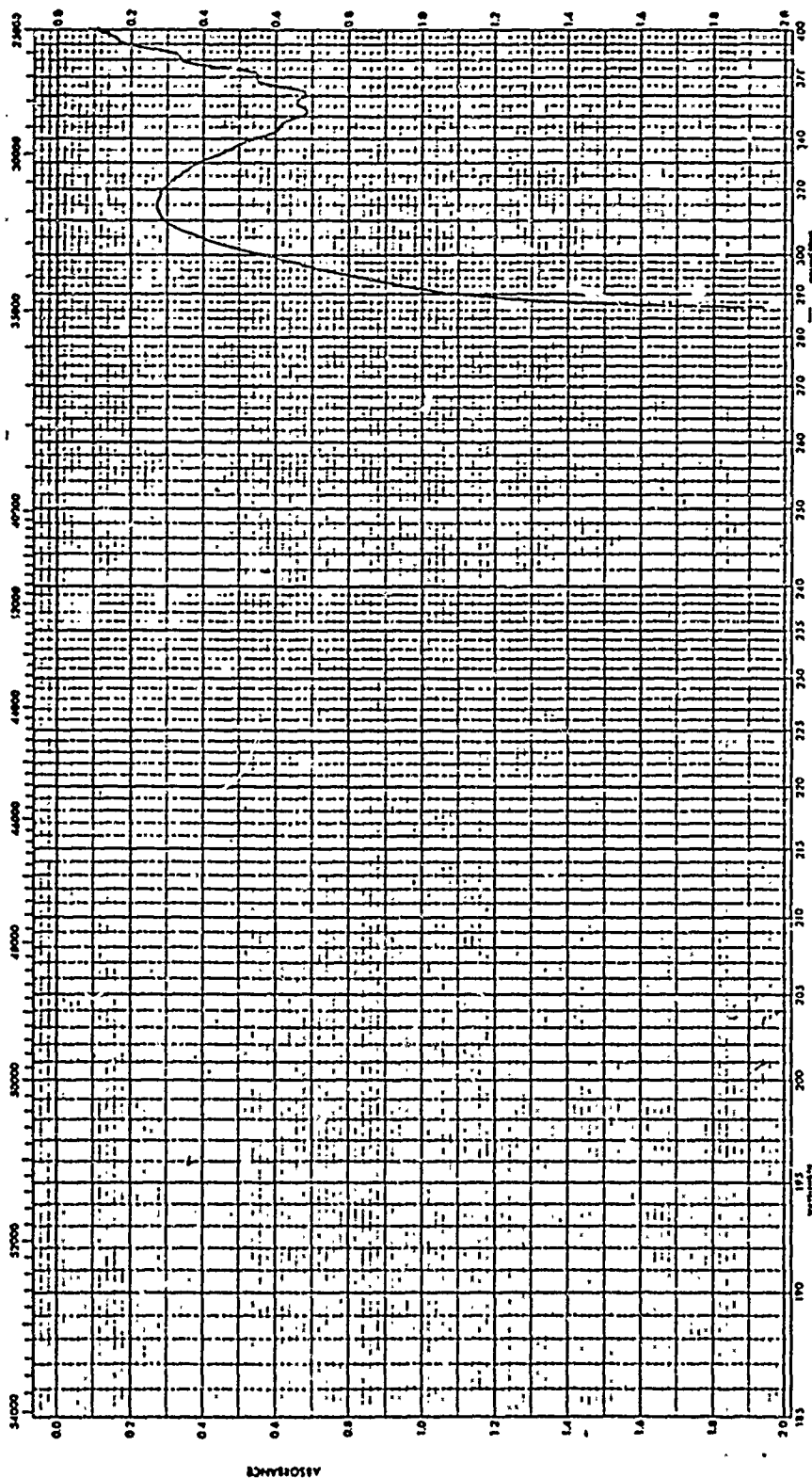


Figure 7. UV Spectrum of Concentrated DBC Complex in Methylene Chloride

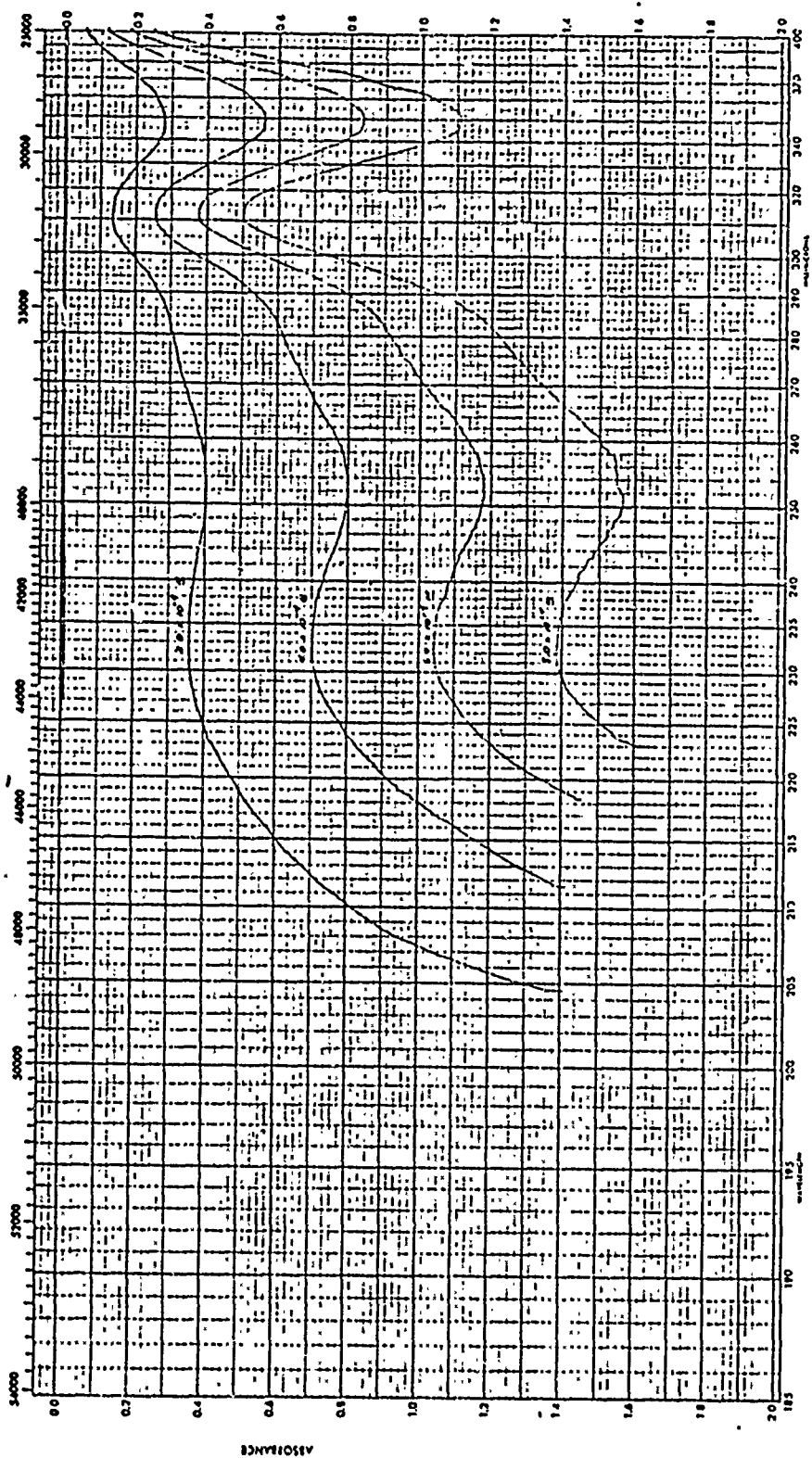


Figure 8. Smooth spectra of Aqueous Potassium Chromate solutions at pH 1, concentrations $2.0 \times 10^{-4} \text{ M}$ to $8.0 \times 10^{-4} \text{ M}$.

to each complexed potassium cation, as opposed to the random order which exists in aqueous solution.

7. TT-E-489F enamel to which small amounts of soluble complexed chromate were added exhibited marked superiority over their unacidified counterparts. in providing corrosion protection to unprimed magnesium, steel, aluminum substrates respectively after 200, 530, and 1680 hours salt spray exposure (as shown in Figures 9-12).

8. After 1680 hours of salt spray exposure, the TT-E-489F enamel containing 0.5 lb/gal AMLchrome (concentrated methylene chloride solution of complexed chromate) exhibited satisfactory adhesion over bare 7075 aluminum when cut with a knife in accordance with Method 6304 of Federal Test Method Standard No. 141, in contrast with the unmodified control or with the enamel containing 0.2 lb/gal AMLchrome which exhibited poor adhesion. This suggests that AMLchrome in the enamel is upgrading adhesion by either providing a chromate treatment similar to MIL-C-81706 pretreatment materials, increasing the polarity of the coating at the coating-substrate interface, or both.

9. In attempting electrodeposition of chromium from organic solvents^{(20) (21)} containing AMLchrome onto copper substrates for the purpose of increasing plating efficiency and reducing hydrogen embrittlement, it was found that none of the plating conditions examined produced anything other than a grayish, dark green scum which was easily removed by rinsing and brushing with a nylon pad.

DISCUSSION OF RESULTS

1. This appears to be the second time in the chemistry of macrocyclic complexation agents where the complexation in solution is pH sensitive⁽²²⁾ and the first time that an inverse relationship has been demonstrated to exist.

(20) D. J. Levy and W. R. Momyer, *Plating*, 57, 1125-31, November (1970)

(21) D. J. Levy and W. R. Momyer, *J. Electrochem. Soc.*, 118, 1563-70, October (1971)

(22) B. Dietrich, J. M. Lahn, and J. P. Sauvage, *Tetrahedron Lett.*, 2885 (1969)

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Figure 9. Enamel Coated Magnesium after 200 hours at 5% Salt Spray Exposure;
A - No additive; B - 0.2 lb/gal AMLchrome; C - 0.5 lb/gal AMLchrome.



Figure 10. Enamel Coated Steel after 200 hours of 5% Salt Spray Exposure;
A - No additive; B - 0.2 lb/gal AMLchrome; C - 0.5 lb/gal AMLchrome.

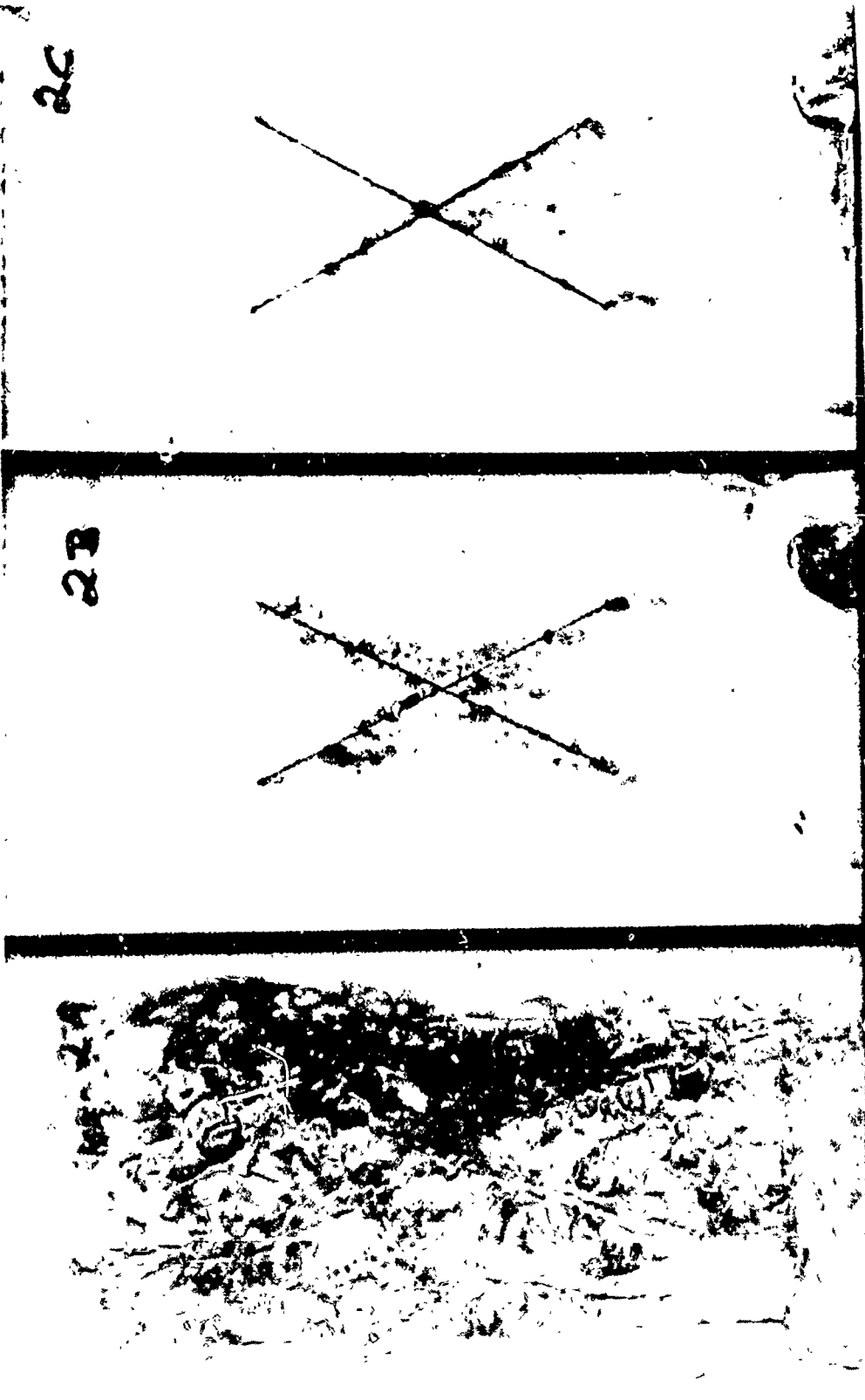


Figure 11. Enamel Coated Steel after 530 hours of 5% Salt Spray Exposure;
A - No additive; B - 0.2 lb/gal AMLchrome; C - 0.5 lb/gal AMLchrome

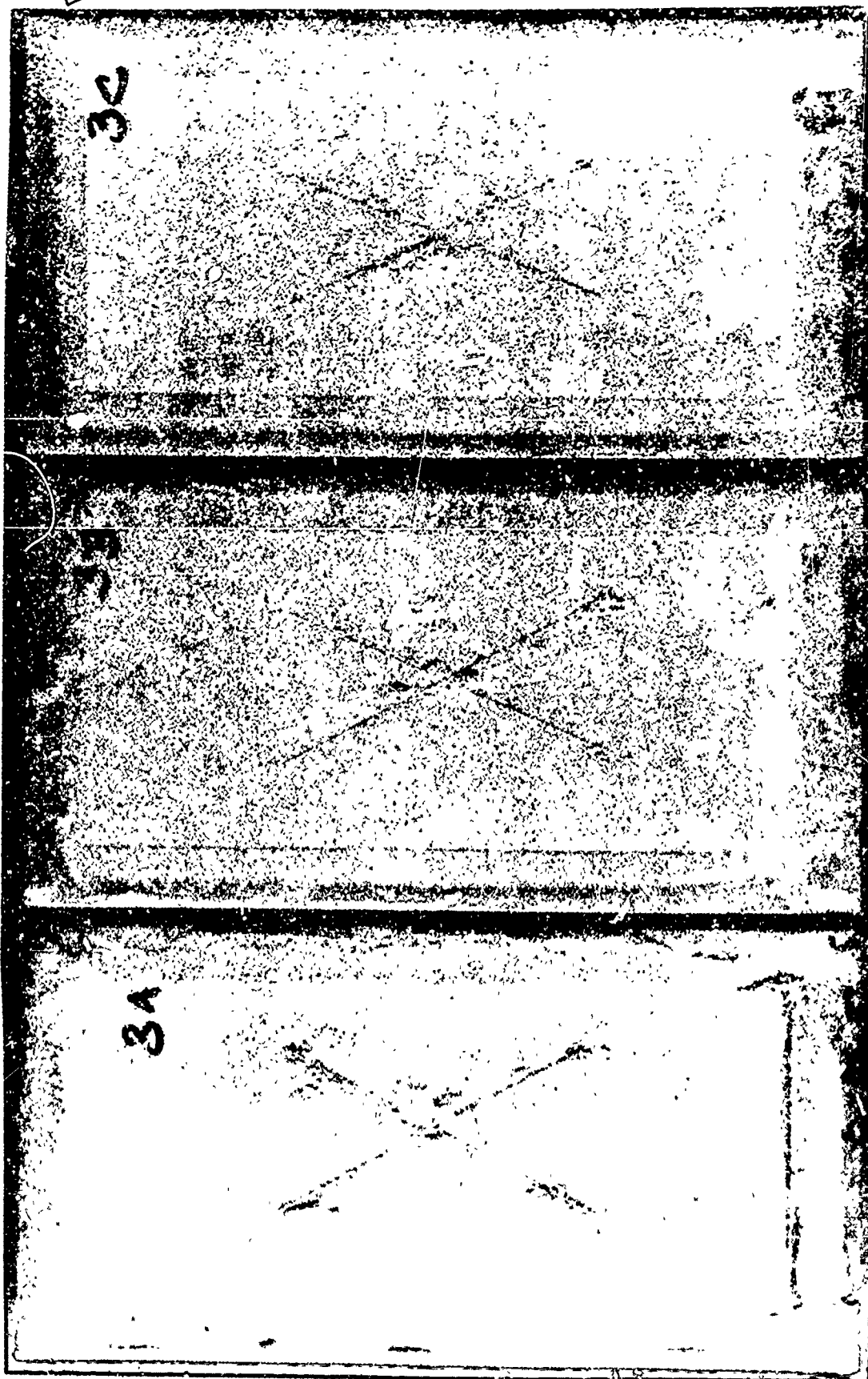


Figure 12. Enamel Coated Aluminum after 1680 hours of 5% Salt Spray Exposure;
A - No additive; B - 0.2 lb/gal AMLchrome; C - 0.5 lb/gal AMLchrome.

It has recently been reported that bicyclic polyethers containing bridge atoms (Figure 13) have complexing properties even more remarkable than the all-polyether types and with the same cations.⁽²²⁾ Complexation in solution with these bicyclics has been found to be a direct function of the pH. Since the cation is presumed to be held in the cavity of the bicyclic by the negative dipole charges of the six oxygen and two nitrogen atoms, it is reasonable to assume that protonation of the amino nitrogen atoms inhibits complex formation because of the repulsion between the two positively charged nitrogen sites and the cation. The rationalization for the pH sensitivity of bicyclic-salt systems is seen to center on the strength of complexation with the cation. Such is not the case when dealing with strict polyethers (DEC and DCC). It is proposed that the pH dependence of Cr +6 solubility, as noted in Result 3, is best explained on the basis of the anion. The following develops that line of reasoning.

2. Result 3 states that the maximum degree of complexation occurs when one mole of polyether solubilizes one mole of Cr +6 anion. In addition, only one cation is suitable for complexation—the potassium +1 ion—which, at 100% complexation, is assumed to occupy the center of the macrocycle of each polyether molecule. Thus, it follows that the only possible species of Cr +6 which may enter into complexation are those which possess a valence equal to the number of Cr +6 atoms in the species—i.e., HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$. Spectrophotometric evidence indicates that the anionic partner is HCrO_4^- : the peak absorbance of Cr +6 in organic solution occurs at 357 nm with a molar extinction coefficient of 1160; HCrO_4^- (aq) has a peak absorbance at 350 nm with a molar extinction of 1600⁽²³⁾; the peak absorbance of $\text{Cr}_2\text{O}_7^{2-}$ (aq), however, occurs at 360 nm with an extinction coefficient (per mole of Cr+6) of 1940⁽²³⁾.

Although non-availability of activity coefficients prevents calculation of Cr +6 species concentrations at high levels of Cr +6 (specifically at 0.5 M—the aqueous concentration from which the Cr +6 species was extracted by complex formation), it seems likely that the pH dependence of complexation is the result of a changing species distribution in the aqueous phase.

←

(23) H. G. Linge and A. L. Jones, Aust. J. Chem., 21, 2189 (1968)

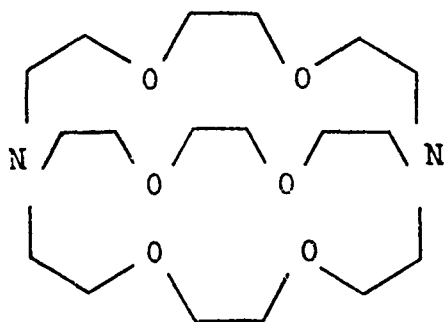


Figure 13. A Macroheterobicyclic Diamine

3. Three explanations are proposed for the preference of the polyether—potassium cation for the bichromate anion to the exclusion of other Cr +6 species. First, HCrO_4^- is more compatible with the "soft" acid cationic system of complexed potassium than $\text{Cr}_2\text{O}_7^{2-}$ since bichromate is a "softer" base; i.e., it has a smaller charge to size ratio. Second, compatibility between bichromate and polyether is increased by virtue of hydrogen bonding between the proton of HCrO_4^- and the ether oxygen of the macrocycle. Such association was recently demonstrated between HBr and DCC.⁽²⁴⁾ Note that the oxygen atom bonded only to aliphatic carbon atoms will be more basic than those bonded to an aromatic carbon, and hence, will be the prime candidate for H-bonding. Third, interaction between the anion of the complexes and the nonpolar solvent should become more favorable with a decrease in the charge density of the ion and an increase in its polarizability. Accordingly the univalent bichromate should be favored in this connection over the "harder" similar sized divalent chromate. (In addition, the bichromate anion gives rise to a simple one cation to one anion configuration, whereas, dichromate requires an entropically less favored system of two cations to one anion.)

EXPERIMENTAL

1. Instrumentation

A Perkin-Elmer UV-VIS-NIR Spectrophotometer Model 450 was used for the determination of hexavalent chromium (Cr +6). A Perkin-Elmer 303 Atomic Absorption Spectrophotometer was employed for the same purpose as an independent check. A Beckman Zeromatic SS-3 pH Meter was used for pH determinations of aqueous Cr +6 solutions.

2. Chemicals

All inorganic compounds and organic solvents were reagent grade commercial products used without further purification. Dicyclohexyl-18-crown-6 was obtained as a courtesy sample from Dr. Frensdorff of the DuPont Co. and

(24) E. Shehori and J. Jagur-Grodzinski, J. Am. Chem. Soc., 94, 7957 (1972)

purified chromatographically with an acid washed alumina column. Dibenzo-18-crown-6 was purchased from the Aldrich Chemical Co. and purified by recrystallization from methanol.

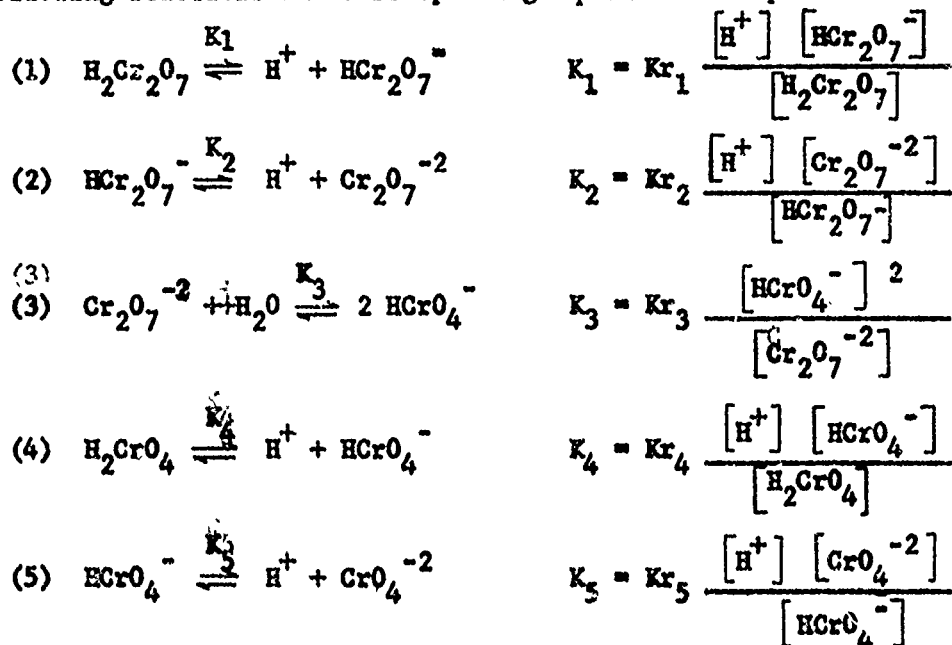
3. Preparation of the Complex

In a typical experiment, a 0.5 M aqueous Cr +6 solution is prepared by weighing 9.71 grams of potassium chromate into a 100 ml volumetric flask, adding distilled water to within 3 ml of full volume, adjusting to the desired pH with concentrated HCl, completing the volume with distilled water and taking a final pH measurement of the solution. Next prepared is a 10^{-2} M stock solution by dissolving the appropriate amount of polyether in a 100 ml volumetric flask with methylene chloride. From this a 10^{-3} M solution is prepared by a 1:10 dilution into a second 100 ml volumetric flask with methylene chloride. Equal volumes (20 ml) of aqueous Cr +6 solution and the 10^{-3} M polyether solution are agitated thoroughly by hand for one minute in a 60 ml separatory funnel and the phases allowed to separate. The organic phase which contains the complex is removed for analysis.

4. Determination of Complexed Cr +6

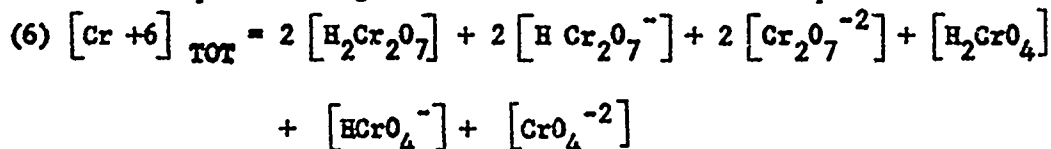
a. Equilibrium of Cr +6 Species in Aqueous Solution

Equilibrium of the various Cr +6 species in aqueous solution is governed by the following reactions and corresponding equilibrium expressions:



Values for the equilibrium constants are those obtained by Linge and Jones. ⁽²²⁾

These five equations together with the mass balance equation:



permit calculation of the concentration of each species for low total Cr +6 concentrations (since at low concentration activity coefficients approach 1.0 and $K_r \rightarrow 1$) and pH. Such calculations have been accomplished for pH values ranging from 0.5 to 9.0 and various Cr +6 concentrations by means of a computer-programmed successive approximation technique. Results for the major species HCrO_4^- , CrO_4^{2-} , and $\text{Cr}_2\text{O}_7^{2-}$ are listed in Table I as functions of the total Cr +6 present. From this data it can be seen that if the extinction coefficients of the Cr +6 species are different from each other (and indeed they are, as determined by Linge and Jones) ⁽²²⁾ then the collective extinction coefficient, as defined in Part C of this section, will depend on both the pH and to some extent on the total Cr +6 concentration. This dependence (experimentally determined by spectrophotometric measurements of various Cr +6 solutions) is plotted in Figure 14.

b. Analysis by Extraction

Ten (10.0) ml of the organic solution containing the complex is pipetted into a 50 ml separatory funnel containing 20.0 ml distilled water and the solutions shaken to decompose the complex and quantitatively extract all the Cr +6. Upon separation of the phases, the light yellow aqueous phase (Solution #3) is examined for pH and absorbance in the 300-400 nm region. Several experimental runs checked also by atomic absorption spectroscopy verified the Cr +6 concentrations as determined by the simpler UV spectrophotometric method.

c. Calculations

Equation (1) defines what shall herein be referred to as the collective extinction coefficient.

TABLE I - CONCENTRATION DISTRIBUTION OF Cr +6 SPECIES AS
A FUNCTION OF PH AND TOTAL Cr +6 CONCENTRATION

TOTAL CHROMIUM CONCENTRATION = .00200 MOLAR						
PH	HCR04	CR04	CR207	H2CR04	HCR207	H2CR207
.50	.151E-03	.155E-09	.776E-05	.478E-04	.245E-06	.776E-07
1.00	.180E-03	.585E-09	.110E-05	.180E-04	.110E-06	.110E-07
1.50	.191E-03	.196E-08	.124E-05	.604E-05	.392E-07	.124E-08
2.00	.195E-03	.635E-08	.130E-05	.195E-05	.131E-07	.130E-09
2.50	.197E-03	.202E-07	.131E-05	.622E-06	.416E-08	.131E-10
3.00	.197E-03	.640E-07	.132E-05	.197E-06	.132E-08	.132E-11
3.50	.197E-03	.202E-06	.132E-05	.623E-07	.417E-09	.132E-12
4.00	.197E-03	.639E-06	.131E-05	.197E-07	.131E-09	.131E-13
4.50	.195E-03	.201E-05	.130E-05	.617E-08	.410E-10	.130E-14
5.00	.191E-03	.620E-05	.124E-05	.191E-08	.124E-10	.124E-15
5.50	.180E-03	.185E-04	.110E-05	.568E-09	.347E-11	.110E-16
6.00	.151E-03	.489E-04	.771E-05	.151E-09	.771E-12	.771E-18
7.00	.466E-04	.151E-03	.738E-07	.466E-11	.738E-14	.738E-21
7.50	.176E-04	.181E-03	.105E-07	.555E-12	.332E-15	.165E-22
8.00	.596E-05	.194E-03	.121E-08	.596E-13	.121E-16	.121E-24
8.50	.195E-05	.200E-03	.129E-09	.615E-14	.407E-18	.129E-26
9.00	.615E-06	.200E-03	.129E-10	.615E-15	.129E-19	.129E-28

TOTAL CHROMIUM CONCENTRATION = .000400 MOLAR						
PH	HCR04	CR04	CR207	H2CR04	HCR207	H2CR207
.50	.299E-03	.308E-09	.305E-05	.947E-04	.965E-06	.305E-06
1.00	.356E-03	.116E-08	.431E-05	.356E-04	.431E-06	.431E-07
1.50	.376E-03	.387E-08	.481E-05	.119E-04	.152E-06	.481E-08
2.00	.385E-03	.125E-07	.504E-05	.385E-05	.504E-07	.504E-09
2.50	.388E-03	.399E-07	.511E-05	.123E-05	.162E-07	.511E-10
3.00	.399E-03	.126E-06	.514E-05	.389E-06	.514E-08	.514E-11
3.50	.389E-03	.399E-06	.514E-05	.123E-06	.162E-08	.514E-12
4.00	.388E-03	.126E-05	.511E-05	.388E-07	.511E-09	.511E-13
4.50	.385E-03	.396E-05	.504E-05	.122E-07	.159E-09	.504E-14
5.00	.376E-03	.122E-04	.481E-05	.376E-08	.481E-10	.481E-15
5.50	.356E-03	.366E-04	.431E-05	.113E-08	.135E-10	.431E-16
6.00	.299E-03	.972E-04	.304E-05	.299E-09	.304E-11	.304E-17
7.00	.931E-04	.303E-03	.295E-05	.931E-11	.295E-13	.295E-20
7.50	.351E-04	.361E-03	.420E-07	.111E-11	.133E-14	.420E-22
8.00	.119E-04	.388E-03	.484E-08	.119E-12	.484E-16	.484E-24
8.50	.389E-05	.400E-03	.515E-09	.123E-13	.163E-17	.515E-26
9.00	.123E-05	.400E-03	.515E-10	.123E-14	.515E-19	.515E-28

TOTAL CHROMIUM CONCENTRATION = .000600 MOLAR

PH	HCR04	CR04	CR207	H2CR04	HCR207	H2CR207
.50	.446E-03	.458E-09	.676E-05	.141E-03	.214E-05	.676E-06
1.00	.529E-03	.172E-08	.951E-05	.529E-04	.951E-06	.951E-07
1.50	.556E-03	.571E-08	.105E-04	.176E-06	.332E-06	.105E-07
2.00	.559E-03	.185E-07	.110E-04	.569E-05	.110E-06	.110E-08
2.50	.573E-03	.589E-07	.112E-04	.101E-05	.354E-07	.112E-09
3.00	.575E-03	.187E-06	.112E-04	.575E-06	.112E-07	.112E-10
3.50	.575E-03	.591E-06	.112E-04	.182E-06	.355E-08	.112E-11
4.00	.573E-03	.186E-05	.112E-04	.573E-07	.112E-08	.112E-12
4.50	.569E-03	.585E-05	.110E-04	.180E-07	.349E-09	.110E-13
5.00	.556E-03	.181E-04	.105E-04	.556E-08	.105E-09	.105E-14
5.50	.529E-03	.544E-04	.953E-05	.167E-08	.301E-10	.953E-16
6.00	.446E-03	.145E-03	.677E-05	.446E-09	.677E-11	.677E-17
7.00	.140E-03	.453E-03	.662E-05	.140E-10	.662E-13	.662E-20
7.50	.527E-04	.541E-03	.944E-07	.167E-11	.298E-14	.944E-22
8.00	.179E-04	.582E-03	.109E-07	.179E-12	.109E-15	.109E-23
8.50	.584E-05	.800E-03	.116E-08	.185E-13	.367E-17	.116E-25
9.00	.185E-05	.600E-03	.116E-09	.185E-14	.116E-18	.116E-27

TOTAL CHROMIUM CONCENTRATION = .000800 MOLAR

PH	HCR04	CR04	CR207	H2CR04	HCR207	H2CR207
.50	.580E-03	.596E-09	.114E-04	.183E-03	.361E-05	.114E-05
1.00	.699E-03	.227E-08	.166E-04	.699E-04	.166E-05	.166E-06
1.50	.740E-03	.760E-08	.186E-04	.234E-04	.588E-06	.186E-07
2.00	.748E-03	.243E-07	.190E-04	.748E-05	.190E-06	.190E-08
2.50	.754E-03	.775E-07	.193E-04	.238E-05	.611E-07	.193E-09
3.00	.755E-03	.245E-06	.194E-04	.755E-06	.194E-07	.194E-10
3.50	.755E-03	.776E-06	.194E-04	.239E-05	.614E-08	.194E-11
4.00	.754E-03	.245E-05	.193E-04	.754E-07	.193E-08	.193E-12
4.50	.748E-03	.769E-05	.190E-04	.237E-07	.632E-09	.190E-13
5.00	.740E-03	.240E-04	.186E-04	.740E-08	.186E-09	.186E-14
5.50	.700E-03	.719E-04	.167E-04	.221E-08	.527E-10	.167E-15
6.00	.584E-03	.190E-03	.116E-04	.584E-09	.116E-10	.116E-16
7.00	.186E-03	.804E-03	.117E-05	.186E-11	.117E-12	.117E-19
7.50	.702E-04	.722E-03	.108E-05	.222E-11	.530E-14	.168E-21
8.00	.239E-04	.775E-03	.194E-07	.239E-12	.194E-15	.194E-23
8.50	.778E-05	.800E-03	.206E-09	.246E-13	.052E-17	.246E-25
9.00	.246E-05	.800E-03	.205E-09	.246E-14	.205E-18	.206E-27

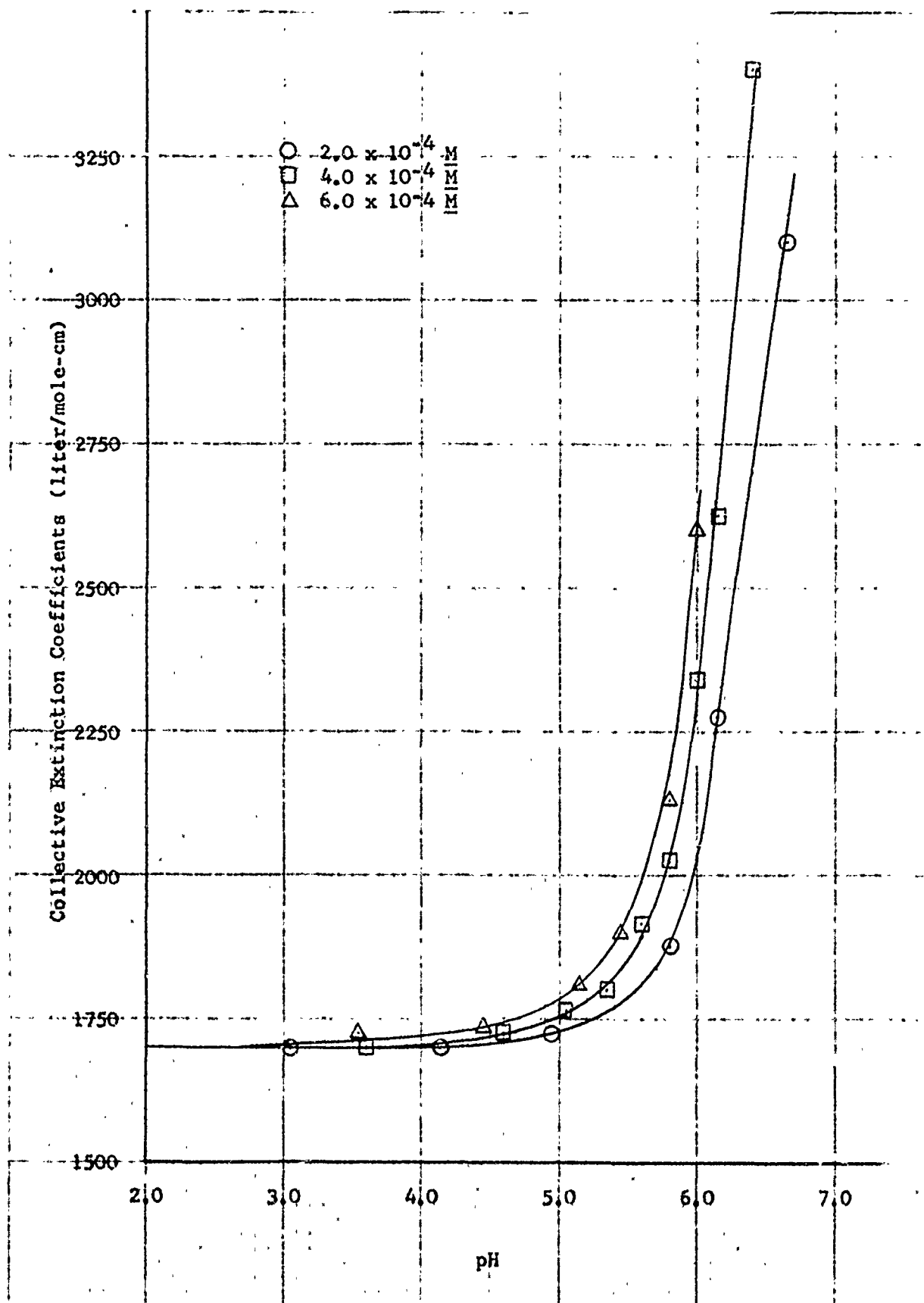


Figure 14. Collective Extinction Coefficients of Potassium Chromate as functions of pH and concentration.

(1) $A_{\text{tot}} = a_c b c$; where

A_{tot} = absorbance of Cr +6 solutions

b = cell path length

a_c = collective extinction coefficient

c = total Cr +6 concentration

The curves of Figure 14 represent solutions to equation (1) for three concentrations of aqueous potassium chromate solutions and varying pH conditions. From Figure 14 it is apparent that a_c is not only a function of pH (because of different Cr +6 species existing at different acidity levels), but also of the total Cr +6 concentration. For this reason, total Cr +6 concentration of an unknown must be determined by a trial and error process which is illustrated in the following example. Solution #3 has been found to have a pH of 5.2 and $A_{\text{tot}} = 0.32$. As a first guess, let c (total Cr +6) = 4.0×10^{-4} M. From Figure 14 the extinction coefficient, a_c , which corresponds to this concentration and pH has a value of 1775. This a_c is now employed to check on the validity of the initial guess:

$$c = \frac{A_{\text{tot}}}{a_c b} = \frac{0.32}{1775} = 1.8 \times 10^{-4} \text{ M}$$

The large discrepancy between the initial guess and the calculated value invites a second trial, this time using 1.8×10^{-4} M as the guessed value. Continued recalculation using this procedure will converge on the true value 2.0×10^{-4} M. Since the concentration of Cr +6 in the organic phase must be twice that of Solution #3 (10.0 ml of the organic phase was extracted with 20.0 ml water), the organic concentration is 4.0×10^{-4} M. Having determined the maximum Cr +6 uptake by the polyether to be one mole Cr +6 per mole polyether, the per cent complexation is calculated as follows:

$$\frac{\text{Conc. Cr +6 in organic} \times 100}{\text{Conc. polyether in organic}} = \frac{4.0 \times 10^{-4}}{10^{-3}} \cdot 100 = 40\%$$

5. Practical Application - Wet Paint Additive

a. Preparation of Panels

Six of each of the following 3 x 6 inch substrates were prepared by first

abrading the surfaces with a fine abrasive mat (MIL-A-9962A, Type I, Class I) and then degreasing the panels by immersion in hot mineral spirits followed by boiling methanol (100%). They were then air dried and placed in a desiccator until required.

<u>Code No.</u>	<u>Substrate</u>	<u>Specification</u>
1	Magnesium alloy	QQ-M-44
2	Mild Steel	MIL-S-7952
3	Aluminum 7075 (Unclad)	QQ-A-250/2

b. Preparation of Chromate Complex Concentrate (AMLchrome)

Dissolved in 200 ml of methylene chloride was 14.7 grams of Dicyclohexyl-18-crown-6 (a 0.2 M solution). This solution was used to extract 200 ml of a saturated aqueous potassium chromate solution which had been adjusted to a pH of 1.0. A one ml portion of the separated phase indicated 61% complexation when analyzed in accordance with Part 4 above. (Note: this is not to be confused with the 100% complexation achieved with the 10^{-3} M concentration of DCC as shown in Figure 6.) The balance of the organic phase was concentrated in a rotary evaporator at 22°C/5 mm, and the syrupy residue thinned with methylene chloride to form a 67% concentrate (AMLchrome).

c. Modification of Enamels with AMLchrome

A white gloss TT-E-489F enamel was modified at two levels with AMLchrome. In modification "B" 5.4 grams AMLchrome was mixed with 140 ml of paint (0.2 lb/gal). In modification "C", 13.5 grams of AMLchrome was mixed with 140 ml of paint (0.5 lb/gal). Specimen "A" was the unmodified paint for use as a control. Modifications B and C were made within 15 minutes of spray application to the unprimed substrates described above. Each of the three coatings were applied in duplicate. The dry film thicknesses were 2.2, 3.0, and 2.6 mils for sets A, B, and C respectively. Coatings were air dried at room temperature for two weeks, then scribed with an "X" through to the substrate metal, sealed on the reverse side, and waxed at the edges. The panels were then placed in a 5% salt fog chamber in accordance with Method 6061 of Federal Test Method Standard No. 141, except that panels

were inclined at six degrees to the vertical. The specimens were examined periodically for evidence of corrosion in the area of the scribe and for integrity of the coating.

6. Attempted Application - Chrome Plating from Organic Solution

Methylene chloride plating solutions are prepared by extracting a saturated aqueous solution of potassium chromate at low pH with a methylene chloride solution of DCC. An N,N-dimethyl formamide solution is prepared by stripping methylene chloride from its solution of the Cr +6 complex at 20°C/2.5 mm. DMF is then added to the residue to the desired concentration.

A cylindrical platinum screen anode (radius = 2.8 cm) is placed concentric to one of two solid copper cathodes (radii = 1.9 and 0.95 cm). The desired voltage is applied to the electrodes which are subsequently immersed in the plating solution where agitation is maintained throughout the plating period. Conditions of each experiment are listed in Table II.

FUTURE WORK

The polyether 18-Crown-6 (see Figure 15) is reported to complex the potassium ion even better than DCC. In addition, it should exhibit increased solubility in nonpolar solvents over DCC. For these reasons, it is planned to synthesize this compound within FY-74.⁽²⁵⁾ Chromate complexes of the macrocycle will be tested in paint topcoats and, if possible, lubricant systems. Work with paint topcoats will be expanded to aircraft lacquers. Included therein will be the determination of the degree of yellowing in white topcoats as a result of AMLchrome in the dry films. The weatherability of such systems will be evaluated. Finally, AMLchrome will be evaluated as a corrosion inhibitive pretreatment for metal surfaces prior to painting. This experiment is important in view of the upgraded adhesion imparted to TT-E-489F enamels by AMLchrome, as described in Results.

R. N. Greene, Tetrahedron Lett., No. 18, 1793-6 (1972)

TABLE II - EXPERIMENTAL PLATING CONDITIONS USING AMLCHROME BATH

<u>Run</u>	<u>Solvent</u>	<u>DDC Conc. (M)</u>	<u>Area Ratio: Anode/Cathode</u>	<u>V (volts)</u>	<u>I/A (ma/cm²)</u>
1	CH ₂ Cl ₂	0.134	1.2	11	16
2	"	0.067	"	23	45
3	"	"	"	40	23
4	"	"	"	40	23
5	DMF	"	"	10	11
6	CH ₂ Cl ₂ *	0.20	6.9	10	21
7	"	"	"	13.5	27
8	"	"	"	40	100
9	"	"	"	60	130

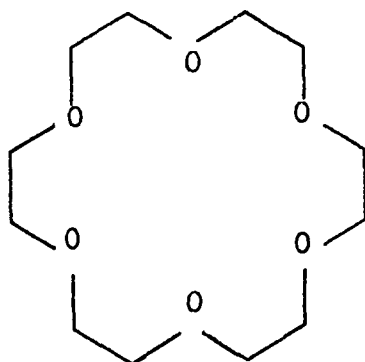


Figure 15. 18-Crown-6

CONCLUSIONS

Methods are presented to enable the solubilization of potassium chromate into wet paint topcoats in concentrations which may be high enough for effective corrosion protection. This is indicated by the superior corrosion protection afforded to the aluminum, steel, and magnesium substrates by enamel topcoats modified by the addition of the hexavalent chromium complex.

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